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Coverage Effects and the Nature of the Metal-sulfur Bond in S/Au(111): High-resolution Photoemission and Density-functional Studies

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Introduction: In general the bonding of sulfur to surfaces of metals is an important topic in catalysis [1], electrochemistry [2], interfacial physics [3], and materials science [4]. Recently, gold has become the subject of a lot of attention due to its unusual catalytic properties when dispersed on oxide supports such as titania [5]. It is important to study the bonding in a sulfur/gold interface and how this system behaves as a function of adsorbate coverage and temperature.

Methods and Materials: The adsorption and reaction of sulfur on a Au(111) single crystal were studied with temperature desorption spectroscopy (TDS), synchrotron-based high-resolution soft X-ray photoelectron spectroscopy (SXPS), and first-principles density-functional (DF) slab calculations.

Results: The interaction between sulfur and gold as a function of coverage and temperature is very complex. At small sulfur coverages, the adsorption of S on fcc hollow sites of the gold substrates is energetically more favorable than adsorption on bridge or a-top sites. Under these conditions, S behaves as a weak electron acceptor but substantially reduces the DOS that gold exhibits near the Fermi edge. As the sulfur coverage increases, there is a weakening of the Au-S bonds (with a simultaneous reduction in the Au→S charge transfer and a modification in the S *sp* hybridization) that facilitates changes in adsorption site and eventually leads to S-S bonding. At sulfur coverages above 0.4 ML, S₂ and not atomic S is the more stable species on the gold surface. Formation of S_n(*n*>2) species occurs at sulfur coverages higher than a monolayer. Very similar trends were observed for the adsorption of sulfur on polycrystalline surfaces of gold. The S atoms bonded to Au(111) display a unique mobility/reactivity not seen on surfaces of early or late transition metals.

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